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The Burning Process in Portland Cement Manufacture.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

DURING the burning process chemical changes occur, the silica, alumina, and iron oxide reacting with the calcium oxide formed by the dissociation of the carbonate to yield calcium silicates, aluminates, and ferrites. These compounds are the main constituents of Portland cement.

Efficient preparation and burning of the slurry are essential to the production of good cement. If the burning temperature is too low, the essential chemical changes are not completed. When properly burned the resulting clinker is a dense grey-black ; lightly burned clinker is soft and yellow to brown in colour. The condition of the kiln atmosphere, whether oxidising or reducing, to a large extent determines the nature of the iron compounds formed. In a reducing atmosphere ferrous oxide is formed and acts as a base, whereas in an oxidising atmosphere the iron is in the ferric state and reacts as an acid. Clinker burned in a reducing atmosphere is unsatisfactory and is of a coffee colour. Clinker which dusts on cooling produces poor-quality cement and may result from one or more of the following causes : (1) non-homogeneous slurry, (2) insufficient lime, (3) burning temperature too low.

Hendrickx [31] considered that the course of clinker formation, that is, the velocity of the several reactions, is infinitely variable, depending on (1) the chemical composition of the raw mixture, (2) the molecular homogeneity of the mixture, (3) the physico-chemical state of the constituents (silica as sand combines much less readily than does soluble silica), (4) the proportion of flux, (5) the temperature maintained in the kiln and the period of burning, (6) the fineness of the raw mixture.

Haegermann[1] illustrated the influence of slurry fineness on burning conditions by the following extreme case. A coarse slurry was divided into two fractions,

namely, those retained and those passing through a 180-mesh sieve. These fractions were heated to the same temperature for the same time. After burning, the finer fraction showed no free lime and the coarser fraction showed 3.16 per cent.

The clinkering of Portland cement slurry involves the following processes: (1) Evolution of mechanical and combined moisture; (2) expulsion of carbon dioxide; (3) Combustion of any organic matter present in the form of peaty matter, bitumen, or other carbonaceous material; (4) Oxidation of ferrous compounds to the ferric state; (5) Oxidation of sulphides, usually ferrous sulphide (FeS) in clays containing organic matter, and pyrites (FeS_2) in rocks and some clays and shales; (6) Partial combination of oxidised sulphur with calcium oxide to form calcium sulphate; (7) Formation of clinker compounds. Less basic lime compounds are first formed. With the appearance of flux the rate of formation of the more basic compounds is increased. The free lime content falls continuously and alite is formed. Chemical reactions are completed by diffusion through the flux. The more refractory constituents are dissolved in the fusible, forming saturated solutions.

Exothermic Reaction of Clinker Formation

During the clinkering process heat is evolved, but the exact amount is a matter of dispute. Richards[3] considered that the combination of the clinker ingredients results in the evolution of a large quantity of heat, equal to 18 per cent. of the heat developed by the combustion of the coal. He deduced this from an experimental heat balance for a 60-ft. rotary kiln. Le Chatelier[4] criticised Richards' calculations and reported that the heat evolved in the exothermic reaction of clinker formation was less than one-half the value given by Richards. Soper[5], [2] gave a value for the heat evolved in clinker formation lower than the value of Le Chatelier. Endell[6], using the method of heat curves, deducted an exothermic reaction commencing at 1,200 deg. C. when slurry was heated. Jesser[7] measured the heat of solution of completely-burnt clinker and also of decarbonated slurry in HCl. He concluded that the reaction of clinker formation was endothermic. Martin and Cooper[2] in summarising the work done on the exothermic reaction of clinker formation indicate that four distinct methods have been used, namely, (1) by determining the heat of formation of the component silicates and aluminates which are considered to form clinker and calculating therefrom the heat of formation of clinker (Richards, Le Chatelier, Dormann, Coghlan); (2) by direct determination in a bomb calorimeter, using charcoal as the source of heat (Tschernobaeff); (3) by means of heat curves (Dittler, National Physical Laboratory, Endell); (4) By solution of the raw materials and clinker in acids and measuring the thermal effects involved (Jesser, Nacken).

Some of the results obtained are given in Table I.

The correspondence of the last two values is remarkably close when we consider that they were obtained by entirely different methods.

TABLE I.

HEAT EVOLVED DURING THE EXOTHERMIC REACTION OF CLINKER FORMATION.

Authority.	Date.	Kilo-Cal. per 100 kilos. clinker.	Method of Determination.	Remarks.
Richards ..	1904	41,430	Calculated from Berthelot's values for the heat of formation of calcium silicates.	Much too high.
Le Chatelier ..	1905	18,560	Calculated from Le Chatelier's value for the heat of formation of calcium silicates.	Too high
Soper	1905	15,870	do. do.	Too high
Tschernobaeff ..	1911	13,350	Direct determination by burning $CaCO_3$ and clay to clinker in a bomb calorimeter.	—
Dormann ..	1914	11,240 to 11,400	Calculated from Tschernobaeff's 1905 determinations of the heat of formation of the calcium silicates and aluminates.	—
Coghlan.. ..	1920	9,916	Calculated from Tschernobaeff and Wologdine's 1912 determination of the heat of formation of the calcium silicates and aluminates.	—
Nacken	1922	10,000	Direct determination by solution of materials in HCl and HF and measuring the thermal changes.	

Expulsion of Combined Water and Decomposition of Clay

Le Chatelier[32] thought the dehydration and decomposition of the clay was completed at 600 deg. C. Cirielli[12] studied the effect of progressive heating of clay marl in an electric furnace and concluded that the water of hydration is completely eliminated by heating at 700 deg. C. The expulsion of combined water from the clay occurs up to 500 deg. C. according to Nacken[13] and the expulsion of combined water from the free silicic acids in the argillaceous material in all probability goes on up to 400 deg. C. Dehydration of silicic acid should be complete at this temperature, but the time factor is important. The expulsion of combined water from the kaolinite contained in the argillaceous material occurs between 450 deg. and 900 deg. C. This process is endothermic, and Tschernobaeff and Wologdine,[8] using the bomb calorimeter, gave

$$H_4Al_2Si_2O_9 = Al_2O_3.2SiO_2 + 2H_2O - 28{,}900 \text{ gr. cal.}$$

Mellor and Holdcroft[14] by means of heating curves gave the value as −10,800 gr. cal. They concluded that the effect of heat on kaolin is as follows: (1) Endothermic reaction, near 500 deg. C., in all probability corresponding with the formation of free silica, free alumina, and water, the two solids forming a very finely divided mechanical mixture. (2) An exothermic reaction, near 800 deg. C., probably corresponding with the polymerisation of the alumina. (3) An exothermic change, near 1,200 deg. C., probably corresponding with the recombination of the silica and alumina formed in the first stage.

Under atmospheric pressure the dehydration of clay is a comparatively slow process. A study of the results of many workers makes it quite clear that completely to dehydrate kaolin in thirty minutes would require a temperature of 800 deg. C.

Expulsion of Carbon Dioxide

Whilst the figures of different authorities vary it is very probable that the evolution of carbon dioxide from a cement raw mixture commences at about 700 deg. C. and is complete at 1,000 deg. C. Table II summarises the figures given by various workers.

TABLE II.

Authority.	Carbon Dioxide Evolution.	
	Commences (deg. C.).	Completed (deg. C.).
Orton[20]	650	1,000
Monath[33]	700	900
Nacken[13]	—	900
Le Chatelier[32]	800	900
Lorenz[34]	—	950

W. B. Newberry[19] stated that carbon dioxide commences to be evolved at 840 deg. C. and is most rapid at 1,030 deg. C. Cirielli[12] reported that the elimination of carbon dioxide takes place rapidly at 800 deg. C.

Formation of Compounds and the Disappearance of Free Lime.

According to Le Chatelier[4], [32] clay and lime commence to react at 800 to 900 deg. C. The reaction becomes more rapid as the temperature rises and the time of burning increases. Cobb showed that the reaction between the lime and the silica begins at about 800 deg. C. Between this temperature and 1,200 deg. C. calcium carbonate, silica, and alumina react to form calcium silicates and aluminates at temperatures much below the eutectic temperature. The incompletely burned and unsintered product is largely soluble in hydrochloric acid. According to Frankforter and Detrick[21] lime reacts with clay when they are heated together at 1,000 deg. C.; the silica and iron oxide of the clay also react together. Nacken[13] stated that lime and clay react to form less basic silicates and aluminates at 900 deg. C. The formation of these lower compounds is completed at 1,200 deg. C. Newberry[19] examined the process of burning by cooling a 60-ft. rotary kiln without emptying it and examined the products at various points in the kiln. He concluded that the reaction starts at 840 deg. C. as shown by a change in colour and a constantly decreasing loss on ignition. According to Bates[22] appreciable amounts of material insoluble in hydrochloric acid only occur in clinkers burned below 1,200 deg. C., i.e., practically all the clay is in combination at this temperature. The amount of material insoluble at this temperature will depend largely on the amount of sand in the clay. Endell[6] and Nacken and Dyckerhoff[35] established that a reaction takes place between the calcium carbonate and clay in slurry even below the dissociation temperature of calcium carbonate, although the extent of the reaction is uncertain. According to Monath[33] and Lorenz[34] the combination of lime, silica, and alumina in slurry has commenced at 700 deg. C. Nacken and Dyckerhoff[35] considered that by far the greater part of the

reactions of clinker formation occur at about 1,250 deg. C. They found that there is a pronounced shrinkage at approximately this temperature in all cement slurries, which is apparently to be attributed to a process of fusion. Nacken[13] stated that the clinkering temperature of Portland cement lies between 1,250 and 1,270 deg. C., and above this temperature the reactions are of a purely physical nature.

Monath[33] followed the course of the reaction in heated cement raw meal to 1,100 deg. C. He determined both the free lime and the carbon dioxide in his burnt samples ; then by calculation he deducted the amount of lime still combined with carbon dioxide and the amount that had already combined with the clay. At about 900 deg. C., i.e., at about the temperature at which the carbon dioxide is completely expelled, almost half of the lime present has already entered into combination. Kühl and Lorenz[24] have confirmed this statement. Lorenz[34] working on similar lines to Monath[33] used three raw meals of the most varied composition which he heated in steps of 50 deg. C. from 700 to 1,500 deg. C. He found that the free lime content falls from about 30 per cent. at 1,000 deg. C. to zero at 1,500 deg. C. It follows from the work of Lorenz that considerable quantities of free lime are still present at 1,250 deg. C., which is the temperature of the shrinkage observed by Nacken. The latter is undoubtedly incorrect when he states that no further chemical change occurs above 1,250 to 1,270 deg. C. ; further reactions involving the combination of lime do occur. Expressed as percentage on the original slurry, Lorenz's figures show about 13 per cent. new compounds formed at 800 deg. C., while this figure becomes 67 per cent. (approximately) at 1,500 deg. C. The course of the disappearance of free lime in a rotary kiln has been followed by Lacey & Woods[23]. They took samples from twelve points along a rotary kiln. As far as the middle of the clinkering zone they could be taken by a ladle ; in the remainder, boxes which could be cleaned and filled were introduced from the outside. The loss on ignition decreases fairly regularly from the back end to the front end of the kiln, but somewhat more rapidly in the lower half of the clinkering zone. The free lime content rapidly increases almost to half way down the clinkering zone and then rapidly decreases. The formation of high basic silicate takes place shortly before the material leaves the kiln.

Course of Reactions with Rising Temperature

First the lime and clay combine to form the less basic silicates and aluminates. Monocalcium silicate ($CaO.SiO_2$) is first produced and its formation predominates between 800 and 900 deg. C. About 900 deg. C. dicalcium silicate ($2CaO.SiO_2$) begins to form. The amount of monocalcium silicate decreases gradually to zero at the expense of dicalcium silicate formation as the temperature rises to 1,100 deg. C. According to Dittler & Jesser[7] the formation of dicalcium silicate is complete at 1,100 deg. C. Kühl and Lorenz[24] and Prüsing [25] state that the formation of dicalcium silicate predominates between 1,000 and 1,250 deg. C. At a temperature about 1,100 deg. C. the aluminate $5CaO.3Al_2O_3$ is produced. At 1,100 to 1,200 deg. C Bates[22] found that only this one aluminate occurs. At

1,200 deg. C. he observed that β-$2CaO.SiO_2$ becomes coloured through taking up iron oxide. At this temperature the compound with refractive index 1.74 (dicalcium ferrite) is noted; at higher temperatures this compound disappears and magnetite is often noted.

The next step is probably the formation of a eutectic. Dittler & Jesser[7], from heating curves of Portland cement slurry, observed an absorption of heat (i.e., fusion of a eutectic) at above 1,250 deg. C. This was also independently observed by Haegermann[1] and by Nacken[13]. The eutectic temperature for the three pure compounds $2CaO.SiO_2$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$ is 1,335 deg. C. (Rankin[36]). In Portland cement slurry, however, are varying quantities of iron oxide, magnesia, and alkalis, and the work of Hansen[27] has shown that these ingredients are powerful fluxing agents. It is therefore probable that a $2CaO.SiO_2$-celite eutectic melts between 1,250 and 1,300 deg. C. (celite here denotes a lime-alumina-iron oxide system of a composition unknown with certainty). Above 1,250 deg. C. Bates[22] noted the disappearance of the $5CaO.3Al_2O_3$. As the temperature rises the amount of flux increases and the rate of formation of tricalcium silicate, from dicalcium silicate and the free lime, increases proportionately. The solid phase contains $3CaO.SiO_2$ and possibly $3CaO.Al_2O_3$, $2CaO.SiO_2$ and CaO. These statements are confirmed by others. Bates[22] says the amount of tricalcium silicate formed increases with temperatures above 1,300 deg. C. Kühl and Lorenz[24] stated that the commencement of partial fusion or sintering at 1,250 deg. C. brings about a rapid decrease in the amount of free calcium oxide, and tricalcium silicate forms at a rate increasing with rise in temperature, the dicalcium silicate decreasing accordingly. Similar conclusions were arrived at by Prüsing[25]. At a temperature between 1,450 and 1,500 deg. C. (depending on the composition of the slurry) the free calcium oxide will have entirely disappeared as a crystalline entity, so that the clinker will then consist of tricalcium silicate and β-dicalcium silicate as crystalline material in contact with a flux saturated with respect to these compounds. Bates[22] states that α-$2CaO.SiO_2$ is only noticed when the temperature reaches 1,500 deg. C.

Clinkering Temperature

The minimum temperature at which good clinker is obtained depends upon (*a*) the chemical composition of the raw mixture, (*b*) the molecular homogeneity of the mixture, and (*c*) the physico-chemical state of the constituents.

Campbell[28] burned many cement raw mixtures of varying composition in an experimental rotary kiln in which temperatures were accurately measured. His conclusions were (*a*) the burning temperature increases with the lime content, and (*b*) the substitution of R_2O_3 for SiO_2, with a very high lime content, is dangerous. Generally speaking, the higher the lime and silica ratios the higher the burning temperature required.

Orton[20] illustrated the influence of the physico-chemical state of the constituents of the raw mixture on the burning temperature. He found that sand requires a higher temperature for reaction with lime than does soluble silica; thus quartz of any size is not attacked until a temperature of 950 deg. C. is reached.

Quartz retained on a 120-mesh sieve is not attacked until a minimum temperature of 1,350 deg. C. is reached. Crystalline calcium carbonate is much more sluggish in reaction compared with the amorphous variety.

In commercial rotary kiln practice coal ash combines with the slurry during burning and, by lowering the lime ratio, lowers the clinkering temperature. Morschitz[29] made measurements of the input and output of two wet-process 164-ft. rotary kilns extending over a week, with analyses of raw meal, coal ash, and clinker. The kiln was free from constrictions and chains. The clinker was found to have absorbed 42.2 per cent. of the total ash of the coal or 7 per cent. of the coal consumed.

Haegermann[1] reported that heating curves of Portland cement slurry indicate that the sintering point lies between 1,250 and 1,290 deg. C. This point corresponds to the Nacken shrinkage temperature, and it has already been pointed out that this is where the formation of eutectic first occurs and not the temperature at which free lime has by any means completely disappeared. Bonde[26] burned portions of the same raw mixture, in a small muffle furnace heated by a blast lamp, to various temperatures indicated by Seger cones. He concluded that 1,500 deg. C. is the most favourable temperature for clinkering. According to Campbell[28] the minimum temperature required to burn clinker to give a sound cement is 1,450 deg. C. Practical experience indicates that the full hardening properties of cement are only developed when the clinker is heated to a temperature exceeding 1,400 deg. C. Kühl[37] has illustrated this point on the manufacturing scale. Holes were bored at several points along a rotary kiln and samples were withdrawn from these holes while the kiln was in motion, the kiln temperatures of the corresponding points lying between 1,200 and 1,430 deg. C. The clinker burnt at 1,430 deg. C. was definitely superior to the less well-burned clinkers.

Influence of Fluxes

Nagai and Asaoka[30] made synthetic mixtures of silica, ferric oxide, and lime in which the ferric oxide content was 10 to 12 per cent. and having lime : silica ratios of 2 : 1 to 3 : 1. Calcium ferrite is the first product formed on heating and it is followed in succession by mono-, di- and tricalcium silicates. A similar result is obtained if part of the iron is replaced by alumina. The authors concluded that the presence of calcium ferrite or aluminate lowers the temperature of formation of tricalcium silicate by 100 to 150 deg. C.

Hansen and Bogue[27] have made an experimental study of the influence of ferric oxide, magnesia, and alkalis on the clinkering temperature of Portland cement slurry. The furnace used was of the Pt-Rd. resistance type, and the mixture under test (all passing a 200 mesh sieve) was contained in a sheet platinum boat fitted into an alundum boat. The furnace tube was more than 2ft. long and the boat moved along this tube at the rate of 1 inch in 2 minutes. Temperature readings were made by thermocouples. The extent of combination was taken as inversely proportional to the percentage of free CaO found in the product by the method of Lerch and Bogue. The basic composition for this study was CaO, 67 per cent., Al_2O_3, 10 per cent. ; SiO_2, 23 per cent.

Various mixtures were then investigated in which a part of the CaO was replaced by MgO, Na_2O, or K_2O, and a part of the Al_2O_3 was replaced by Fe_2O_3. A maximum temperature of about 1,500 deg. C. is required to effect the complete combination of the basic mixture under the present conditions. The speed of the reactions starting with these raw materials may be different from those of practice for the form of the components and the way they may be combined in cement raw mixture greatly influences the rate of combination. Therefore, whilst these results will give valuable indications, they must be applied to practice with reservations. The conclusions which Hansen and Bogue arrived at were:

(1) The following compounds were identified in the clinkers: $3CaO.SiO_2$, $2CaO.SiO_2$, $3Ca.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO.

(2) Effect of replacing CaO by Na_2O and K_2O. These oxides have no special value in increasing the combination of CaO for this composition. Above 1 per cent. of alkali tends to decrease the combination. Probably a given weight of alkali may combine with a larger amount of SiO_2 or Al_2O_3 than does the same weight of CaO. Then the SiO_2 of Al_2O_3 available for combination with the CaO would be decreased with each portion of alkali added and the result would be analogous to the addition of more and more CaO to the mixture.

(3) The replacement of Al_2O_3 by small amounts of Fe_2O_3 or the replacement of CaO by small amounts of MgO aids materially in promoting the combination of lime. The influence of MgO is greater than that of Fe_2O_3, e.g.: (*a*) basic mixture alone, complete combination at 1,500 deg. C.; (*b*) 4 per cent. MgO replacing 4 per cent. CaO, complete combination at 1,350 deg. C. (*c*) 4 per cent. Fe_2O_3 replacing 4 per cent. Al_2O_3, complete combination at 1,410 deg. C.

(4) Replacement by MgO and Fe_2O_3 together are more effective than are replacements by either alone.

(5) In order to obtain the greatest decrease in the temperature required for complete combination with the least change in the original combination the optimum mixture seems to be one in which 3 per cent. of both MgO and Fe_2O_3 replace an equal amount of CaO and Al_2O_3.

Influence of the Degree of Burning and the Rate of Cooling

It is probable that some of the best quality clinkers are those which are burned to a dense or even vitrified condition. The rate of cooling is also an important factor. There have been many indications[38] that rapid cooling of clinker improves its hardening qualities. There are two reasons for this. If alite is tricalcium silicate with a little tricalcium aluminate in solid solution, and if the strength of cement is in proportion to its alite content, then rapid cooling preserves this solid solution to a greater extent than does natural cooling. The other view, which Kühl[38] holds, is that the rapidly-cooled clinker, having had no time to crystallise, possesses a much greater chemical potential than does the slowly crystallised equilibrium product in a similar manner to that of blast-furnace slag.

Rapidly cooled clinkers may be quite different in the nature of the compounds present to the case of slowly cooled clinkers. In this connection Kühl withdrew samples directly from the clinkering zone of a kiln and cooled them rapidly.

They did not possess the colour of normal clinker but were markedly reddish-brown. The same clinker showed the normal colour when it had passed directly through the kiln and cooler without interference. The red colour was thus not due to a reducing atmosphere in the burning zone. Kühl considers that at the temperature of the firing zone some dissociation of iron compounds occurs with the formation of free iron oxide, and the colour of the rapidly-cooled product is due to this oxide. When hot clinker is slowly cooled this free iron oxide has an opportunity to recombine at a somewhat lower temperature, with the result that the red colour of the clinker disappears.

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Tests on a Mill with Air Separator. By F. Prockat, E. Rammler, and W. Müller (*Tonindustrie-Zeitung*, Nos. 11 to 15, 1934).—The relations between feed, power requirement, and fineness were determined, and the influence of air separation on the grinding process examined. It was shown that Rittinger's law held good for this type of mill. Further tests showing the effect of the size of the charge on the grinding are being carried out.

The Grinding of Cement Clinker.

By RUDOLF ZOLLINGER.

THE question of the best degree of grinding for cement has not yet been decided. Theoretically, the quality of cement should improve with increasing fineness, and, generally speaking, this is the case, as is shown by test results given in Table I. The figures in the table refer to one cement ground to different degrees of fineness under the same conditions.

TABLE I.

Per cent. residue on 180-mesh sieve.	Tensile strength in lb. per sq. in. at			Crushing strength in lb. per sq. in. at		
	3 days.	7 days.	28 days.	3 days.	7 days.	28 days.
10	260	313	370	2,332	2,915	4,050
8	242	350	420	2,332	5,517	6,826
6	271	317	459	1,905	4,749	7,650
4	336	398	441	2,403	5,916	7,537
2	299	378	483	5,162	6,783	7,906
1	—	404	526	—	5,873	9,954
0	359	449	530	5,930	7,224	9,499

In many cases, however, an increase of fineness above a certain limit causes a reduction in strength, which varies for different cements, i.e., with some cements the reduction sets in earlier than with others. It is thus necessary to determine the most favourable fineness in each case. In the case of cement raw materials fineness cannot be taken too far, and its limit is only determined by economic considerations, but for cement other factors about which very little has hitherto been known enter into the question.

By the separation of lime with the mixing water a colloidal mass of calcium hydrate is formed in which the residual constituents are embedded. If we consider that with increasing fineness the particles become increasingly more spherical in shape, and that the sphere is the body of minimum surface, it is conceivable that this reduction in the surface of individual particles may be accompanied by a reduction in the power of attack of the mixing water. Thus, setting will be retarded, or may even remain incomplete.

The reduction in strength with continued grinding is most evident with cements in the grinding of which separators have been used. The product of grinding plant employing methods of separation is distinguished from that of the compound mill by a more uniform grain size. The importance of proper grading of the aggregates in the production of strong concrete is well known. In the same way the residual cement forms a "concrete" with the calcium hydrate, which may offer some explanation of this phenomenon.

The theory has been advanced, particularly by Helbig, that the reduction in strength is entirely due to the combination of the finest particles, even before the cement is mixed, with the moisture which is everywhere present. Practical considerations indicate, however, that the explanation lies in the fact that a cement

of mixed grain size gives better strength. Technically, the required conditions are best attained with the compound mill, which, as a result, dominates in grinding cement, while the field of the separator lies in grinding raw materials.

The question of how fine to grind is an economical one in the case both of raw materials and of cement. Cement grinding requires more power than raw materials, and increasing the fineness is only reasonable up to a certain limit. Table I shows that for the cement in question the limit is reached at 1 per cent. residue on the 180-mesh sieve; further grinding to 0 per cent. residue is in this instance waste of power.

While the separator allows practically any fineness to be obtained with the simplest plant, conditions are very different with the compound mill. In this case there is no removal of the finest fraction, and, if this is continuously ground, under certain conditions it becomes dead-ground, in that the grinding media pound it into scales which possess no useful strength.

Fine grinding also affects setting time. At first setting time increases with fineness, but beyond a certain limit of fineness setting time is slowly reduced. It would appear that the heat generated in the mill is the sole cause of this phenomenon. In grinding to increased fineness the mill output is reduced. The thickness of the cushioning material between grinding media and mill plates is less, and there is more working of iron against iron whereby more heat is generated. The temperature may thereby rise to 200 deg. C., with the result that a proportion of the water of crystallisation of the added gypsum will be given up. Since the resulting anhydride has no effect on setting time, the above effect is simply explained.

The grinding mills used for cement are chiefly ball, tube, and compound mills; the two former are generally used with separating devices, and are complementary to each other. More rarely the centrifugal mill is employed, or a form of preliminary mill combined with suitable screening arrangements or with a tube mill behind it.

Since grinding costs are one of the chief factors in cement production it is important to operate the mill at maximum capacity. This may be done by determining the most favourable speed of revolution, the best type and size of grinding media, the best charge of grinding media and clinker, the best period for the material to remain in the various compartments of the compound mill, or the best time for the material to pass from one machine to another in the case of mixed grinding. The conditions vary widely in different cases, and to determine them the grinding curve of the mill must be drawn; this is obtained by the sieve analysis of samples taken at frequent intervals along the mill. The mill conditions are then varied until the curve falls uniformly along the length of the mill.

Fig. 1 shows the grinding surve for a compound mill 11 metres long. It will be seen that the grinding effect is excellent in the first 8m. of the mill, but that the end 3m. contribute nothing. To improve matters in this case the first and second compartments, which are at present doing almost all the work, should be shortened, and the third compartment divided into two; the new third com-

partment should contain somewhat coarser grinding media, and the fourth compartment somewhat finer media. That the first two compartments will stand shortening is shown by the extent to which grinding is driven in these chambers, which proves that they are not completely used but run partly empty, causing

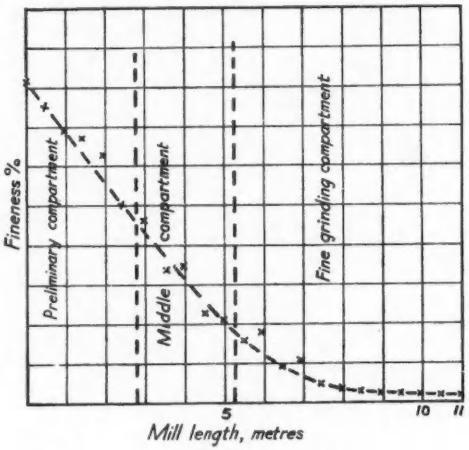

Fig. 1.

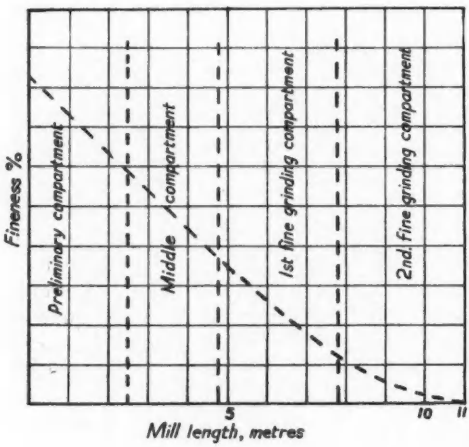

Fig. 2.

excess wear due to the working of iron on iron. The suggested division into four compartments results in the grinding curve of Fig. 2, which shows that the mill is now uniformly used for grinding along its whole length, which is the basic condition for rational grinding.

The System $CaO—SiO_2—H_2O$ at 30° C. and the Reaction of Water on Anhydrous Calcium Silicates.

A RESEARCH paper (No. R.P. 687) with the above title, embodying the results of recent investigations by Messrs. E. P. Flint and Lansing S. Wells, has been issued by the Bureau of Standards of the United States Department of Commerce.

In their introductory remarks, the authors state that an experimental study of the system of lime-silica-water should possess considerable practical value for its direct bearing upon the problem of the setting of Portland cement and hydraulic mortars.

The first part of this paper deals with the solubility relationships of lime and silica, and presents correlations between the compositions of hydrated solid phases and of solutions with which they may exist in equilibrium and with the state of combination of lime and silica in these solutions as determined electrometrically. The paper next considers the reaction of water upon compounds occurring in the binary system, lime-silica, in the light of the foregoing study. These compounds have the molecular proportions[1] $CaO.SiO_2$, $3CaO.2SiO_2$, $2CaO.SiO_2$, and $3CaO.SiO_2$. Tricalcium silicate ($3CaO.SiO_2$) and dicalcium silicate in its beta modification (β — $2CaO.SiO_2$) are the major constituents of Portland cement,[2] in which the gamma form of dicalcium silicate (γ — $2CaO.SiO_2$) also appears occasionally. It is shown that the generalisation of Le Chatelier[3] that hydraulic materials possess metastable solubilities applies to the calcium silicates occurring in Portland cement. Finally the reactions of diatomaceous silica and of silica gel with lime in solution are compared and the relationship of the results to the system $CaO — SiO_2 — H_2O$ is discussed briefly.

The following are the salient points in the paper:

PRELIMINARY STUDY OF THE SYSTEM $CaO — SiO_2 — H_2O$ AT 30° C.—Preliminary experiments showed that silica gel dissolves slowly in dilute calcium hydroxide solutions at 30° C., but that increase of temperature had a marked effect upon its solubility and rate of solution. However, it was found that precipitation of the colloidal silica could be effected quite readily by the addition of a small quantity of saturated calcium hydroxide solution. To investigate further the solubility relationships of silica and lime, a large quantity of the sol-containing solution was prepared, care being taken to avoid contamination by carbon dioxide of the air. The composition of this solution corresponds to

[1] A. L. Day, E. S. Shepherd, and F. E. Wright, The lime-silica series of minerals, *Am. Jour. Sci.*, series 4, vol. 22, p. 265, 1906.

[2] G. A. Rankin, A study of the constitution of Portland cement clinker, *Jour. Ind. Eng. Chem.*, vol. 3, pp. 211–227, 1911; P. H. Bates, The constitution of Portland cement, *Concrete and Cement Age* (Cement Mill Section), vol. 2, pp. 3–4, 1913; G. A. Rankin and F. E. Wright, The ternary system $CaO—Al_2O_3—SiO_2$, *Am. Jour. Sci.*, series 4, vol. 39, pp. 1–79, 1915.

[3] H. Le Chatelier, Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques, Thése, Paris, 1887. English translation by J. L. Mack, New York, 1905.

point A in Fig. 1. This solution was then mixed in various proportions with a calcium hydroxide solution of the composition represented by point B, Fig. 1.

The mixtures, in well-stoppered flasks, were placed directly in an air thermostat[6] maintained at 30 ± 0.05 deg. C. Rapid separation of a part of the lime and silica in the form of voluminous flocculent precipitates occurred as the solutions changed from unstable states to conditions more nearly approaching equilibrium. After one month the solutions were filtered from the precipitates and were analysed for silica and lime, using 400 to 700 ml. samples. Silica was determined by double dehydration, ignition to constant weight followed by volatilisation with hydrofluoric acid and reignition to constant weight. Lime was precipitated as calcium oxalate and ignited to constant weight as the oxide.

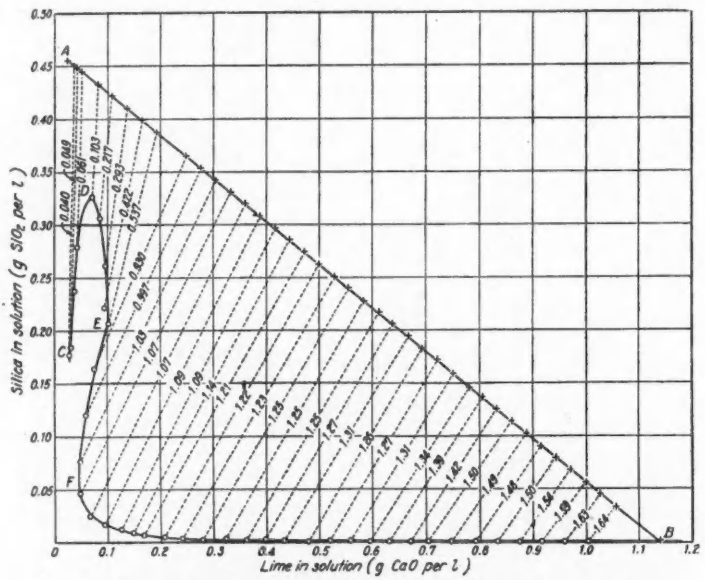

Fig. 1.—Quantity of silica at 30 deg. C. in solutions of increasing lime concentration which are saturated with respect to hydrated solid phases containing lime and silica in the molar proportions shown.

The proportions of lime to silica in the precipitates were obtained from the differences between the compositions of the solutions before and after precipitation.

The results are illustrated by Fig. 1, where the curve CDEFB represents the solubility of silica in solutions containing increasing concentrations of lime. The initial compositions of the unstable lime-silica solutions are represented by points on the diagonal AB. Broken lines from these points to points on the curve CDEFB connect the initial and final compositions. The figures accompanying these lines give the molar ratios of lime to silica in the precipitated

material calculated from the differences between the initial and final compositions of the solutions.

It will be shown later by an electrometric method that of the total lime in solution in the region of the curve CDEF a relatively small proportion is uncombined and that the molar ratios in column 4 very nearly represent the actual state of combination in solution. Thus molar ratios between 0 and 0.5 may represent equilibria between hydrated silica and a calcium silicate containing lime and silica in the molar proportion $1CaO:2SiO_2$. Molar ratios between 0.5 and 1 may represent equilibria between two calcium silicates of molar proportions $1CaO : 2SiO_2$ and $1CaO : 1SiO_2$.

The highest molar ratio of lime to silica in the solid phase indicated in Fig. 1 is 1.64. Thus it appears that the molar ratio $2CaO : 1SiO_2$ is approached when the solid phase is in equilibrium with saturated lime solution. These hydrated calcium silicate precipitates were found to set to a hard mass after drying between filter paper and in a desiccator.

REACTION OF WATER ON MONOCALCIUM SILICATE ($CaO.SiO_2$).—The monocalcium silicate forms apparently stable solutions which may stand for months without appreciable change in composition, differing in this respect from the more basic anhydrous calcium silicates, all of which form metastable solutions capable of spontaneous precipitation. Electrometric measurements, which showed that the molar ratio of combined lime to silica in this region was approximately 0.5, indicated that $Ca(H_3SiO_4)_2$ is the principal product of the hydrolysis of monocalcium silicate. Thus it appears that anhydrous monocalcium silicate cannot be said to have a true solubility but rather one that is incongruent.

REACTION OF WATER ON GAMMA-DICALCIUM SILICATE ($\gamma - 2CaO.SiO_2$).—Dicalcium silicate occurs in cement predominantly in the unstable beta form[4], The reaction of $\gamma - 2CaO.SiO_2$ with water is very similar to that of $3CaO.2SiO_2$ but somewhat more rapid. Both form metastable solutions capable of spontaneous precipitation. Initially the $\gamma - 2CaO.SiO_2$ is hydrolysed, giving solutions containing principally CaH_2SiO_4 as indicated by electrometric measurements.

REACTION OF WATER ON BETA-DICALCIUM SILICATE ($\beta - 2CaO.SiO_2$).—The rate of reaction is much greater than that of $\gamma - 2CaO.SiO_2$ and the solutions formed were more highly supersaturated with respect to the hydrated products. The molar ratios of combined lime to silica in solution given by electrometric measurements showed that the dicalcium silicate gives solutions containing CaH_2SiO_4 with increasing amounts of $Ca_3(HSiO_4)_2$ being formed as the lime concentration increases.

REACTION OF WATER ON TRICALCIUM SILICATE ($3CaO.SiO_2$).—The reaction of water with tricalcium silicate is of great rapidity, as might be expected in the case of such a highly basic compound. Although a saturated lime solution resulted after $4\frac{1}{2}$ hours' contact with the silicate, hydrolysis continued further and a supersaturated solution containing 1.226 g. CaO per litre and 0.0023 g,

[4] See footnote 2.

SiO_2 per litre was produced after 8 hours. It is probable that supersaturation of calcium hydroxide as well as supersaturation of the silicates plays an important part in the setting of Portland cement. The reaction of tricalcium silicate is differentiated from that of the less basic calcium silicates by its much greater rate and the instability of the solutions. The principal products of hydrolysis in the presence of saturated or supersaturated lime solution would be hydrated calcium orthosilicate, $Ca_2SiO_4.nH_2O$, and solid calcium hydroxide. Well-defined crystalline dicalcium silicate is formed by reaction between tricalcium silicate and water at 150 C. and crystalline calcium hydroxide.

REACTION OF WATER ON PORTLAND CEMENT.—Insofar as the calcium silicates are concerned, the reaction of Portland cement with water appears to involve the formation of supersaturated solutions of calcium silicate and subsequently of calcium hydroxide and spontaneous precipitation from such solutions. The results indicate that hydrated calcium orthosilicate, $Ca_2SiO_4.nH_2O$, together with solid calcium hydroxide are products of the reaction of Portland cement with water under usual conditions, the hydrolysis of the former compound being reduced by the supersaturated solution of calcium hydroxide which is formed. Such a process, involving the formation of supersaturated solutions from the anhydrous compounds and the spontaneous precipitation of much less soluble products therefrom, is in agreement with the mechanism of hydraulic reactions first proposed by Le Chatelier.[5] The subsequent setting and hardening may then occur through the withdrawal of water from the hydrated products according to the mechanism suggested by Michaelis.[6]

It may be definitely concluded from the results of this investigation that the calcium silicates occurring in cement are not hydrolysed completely to silicic acid and calcium hydroxide in the presence of a relatively small quantity of water, as has sometimes been stated. Such extensive hydrolysis can occur only when the lime concentration has been reduced to a few hundredths of a gram of CaO per litre, a condition not likely to occur in the setting of Portland cement. Instead, hydrated calcium orthosilicate and calcium hydroxide appear to be the most probable products of the reaction under usual conditions.

New Lightweight Aggregate. By F. Huth (*Tonindustrie-Zeitung*, No. 33, 1934).—A new lightweight aggregate has been produced with a specific gravity of 1·5 and a compressive strength of from 1,400 to 3,500 lb. per square inch. The aggregate is prepared from clay used for ceramic products. The clay is mixed with brown coal or sawdust and formed into balls about 2 cm. diameter. The material is then gradually heated from 100 deg. C. to 300 deg. C. and allowed to cool to 100 deg. C. It is then given a thin coating of unburnt clay, dried, and passed through a rotary kiln 20 metres long, which it enters at 300 deg. C. and leaves at 1,100 deg. C. The proportions used for concrete are four parts light aggregate, 1 part cement, 1 part sand, to which water is added in the proportion of 20 per cent. of the total dry weight of the materials.

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[5] See footnote 3.

[6] W. Michaelis, Recognition of Hydraulic Cements, *Prot. Ver. D.P.C.F.*, 1909.

Waste-Gas Temperatures of Rotary Kilns.—III.

By Dr.-Ing. Rudolf Frey.

Sequence of Stages in the Reduction of the Fuel Consumption.

Besides the determination in figures of the temperature of the waste gas and of fuel consumption, the present work attempts to state in figures the various influences to which the heat consumption of a rotary kiln is subject and to arrange them according to their importance. Three groups of influences on the fuel consumption can be distinguished, namely, technical, operating, and structural causes. The technical influences relate to the height of the clinkering temperature, the water content of the raw material, and the composition and calorific value of the fuel. The operating influences include the maximum combustion temperature (i.e., the extent of the preheating of the air and the excess of air), the daily output, the position of the flame in the kiln, and the presence of flue dust and rings. Structural influences are the dimensions of the rotary kiln, the interior fittings or chains, the inclination of the kiln, its speed of rotation, and the capacity for heat conduction of the kiln lining.

The calculation permits these influences to be arranged according to their value. The sequence is obtained by increasing and decreasing (say, by 1 per cent.) in the calculation in the same proportion each of the influences enumerated and arranging according to their size the variations of the heat consumption found thereby. In addition, separate influences may be followed up over a greater range of the variations. From this follow various conclusions of general value. For the derivation, a normal example with the following details is used: Dimensions of kiln, 3 m. by 60 m.; raw mix, 77·5 per cent. $CaCO_3$, 36·0 per cent. water; daily capacity, normally 200 tons; coal, 6,600 kcal. per kg. calorific value; feed temperature of slurry, 30 deg. C.; temperature of clinker at the outlet of the kiln, 1,050 deg. C.; excess of air, 1·10; maximum theoretical temperature of flue gas, 2,000 deg. C.

From this it follows that:

1 kg. of clinker = 1·53 kg. raw mix and 2·39 kg. slurry
" " = 1·185 kg. $CaCO_3$ and 0·84 kg. water

and the chemical heat requirement.

$$= 1{\cdot}185 \times 425 - 100 = 404 \text{ kcal. per kg. clinker.}$$

The clinkering temperature is as in Fig. 1, i.e., 1,420 deg. C. The outer surface of the kiln is 565 square metres, and the inner surface 500 square metres.

For a normal case the computation of the waste gas temperature is as follows:

(I) DETERMINATION OF THE CURVE OF HEAT REQUIRED.—The constant requirement of the kiln consists of

	kcal.
(*a*) The chemical requirement .. .. =	404
(*b*) The heat required to heat the raw mix to 950 deg. C. $1{\cdot}53 \times 0{\cdot}21 \times (950 - 30)$ .. .. =	296
(*c*) The heat required for further heating to 1,420 deg. C. $1{\cdot}00 \times 0{\cdot}25 \times (1{,}420 - 950)$ .. .. =	118
Constant requirement =	818

At a temperature of the flue gas of	150	300	450	600	750 deg. C.
the shell losses per sq. metre per hour are	1,475	1,900	2,700	4,160	6,150 kcal.
Therefore per kg. clinker q_w =	100	129	183	282	417 kcal.
The ordinates of the curve of heat required are then	918	947	1,001	1,100	1,235 kcal.

(II) THE CURVE OF THE FLUE-GAS HEAT:

Mean temperature difference according to equation (6*a*) ..	292	405	496	574	649 kcal.
Mean heat exchange coefficient, 33·2					
The ordinates of the curve of the flue-gas heat are	582	807	987	1,140	1,290 kcal.

The intersection of the curve of heat required and the curve of the flue-gas heat lies at 480 deg. C. temperature of waste gas. The shell loss is 200 kcal. per kg. clinker. The thermal efficiency is therefore 76 per cent.

The waste-gas temperature of the perfectly insulated kiln would be 310 deg. C.; its efficiency is therefore 84·5 per cent. and the quality coefficient of the kiln 90 per cent.

The fuel consumption with 480 deg. C. waste-gas temperature and 200 kcal. shell loss on the rotary tube according to equation (13) is

$$B = \frac{404 + 262 + 689 + 60 + 200 - 35}{(1 + 0{\cdot}00157 \times 6{,}600) \times (595 - 123)} = 0{\cdot}297 \text{ kcal. per kg. clinker.}$$

The heat consumption is $Q_B = 0{\cdot}297 \times 6{,}600 = 1{,}960$ kcal.

Technical Influences.—Of the influences of a technical nature the composition of the raw mix and the clinkering temperature are of first importance. Without discussing the question whether an alteration of the clinkering temperature might be obtained, there is calculated in the example for its influence the factors $-1{\cdot}80$ and $+8{\cdot}50$; that is to say, an alteration of the clinkering temperature by 1 per cent. upward or downward would result in a change of the heat consumption by 8·5 and 1·80 per cent., that is, from 1,960 to 2,100 respectively to 1,925 kcal. per kg. clinker. In this description of the influence by means of factors the negative sign in front of the factor always denotes the direction of lower fuel consumption and the positive sign the direction of higher fuel consumption.

Already in this case there is seen a peculiarity which will arise again later, namely, that an increase of the normal cardinal numbers has a greater effect on the fuel consumption than a decrease of equal extent.

In comparison with other kilns the computed factor is high, and this is a typical sign of the fact that the kiln is relatively overloaded. The curve of the heat required and that of the flue-gas heat then intersect at a very sharp angle, and the shifting of the point of intersection, particularly upward, becomes considerable from a slight cause. The other factors which result will

also be high, but they remain in the same sequence as for a kiln with a smaller load.

The influence of the water content in the raw mix takes second place amongst the technical data. In the present case it has the factor $-0{\cdot}5 + 0{\cdot}6$, which is very small compared with the clinkering temperature. It is naturally dependent on the normal water content of the raw mix, and with a very great water content it can reach $\pm 1{\cdot}0$; on the other hand, for the dry process it can amount to only $\pm 0{\cdot}1$. For the kiln examined here a change of the water content would have the following effect :—

Water content of the raw mix ..	10	20	30	40	50 per cent.
Heat required by kiln	1,284	1,505	1,780	2,180	2,665 kcal.
Factor of the water content ..	$\pm 0{\cdot}12$	$\pm 0{\cdot}29$	$\pm 0{\cdot}42$	$\pm 0{\cdot}50$	$\pm 0{\cdot}56$

For low water content the factor drops to that of the third influence, namely, the calorific value of the coal. The influence of the calorific value of the coal is so slight that a fluctuation of 1 per cent. cannot be followed further in the calculation; only the fact that a change of ± 10 per cent. would vary the heat required by ± 18 kcal., that is 0·92 per cent., allows the factor for the calorific value to be fixed at about $\pm 0{\cdot}09$. This shows the justification for stating the heat consumption of a kiln in kcal. per kg. clinker, and that the question as to the most favourable coal must not be treated from the standpoint of the calorific value. Without risk of making a considerable error, one may therefore calculate with a normal coal of about 7,000 kcal., and later compute the weight of the coal from the heat required by division with the calorific value.

Still smaller than the influence of the calorific value is that of the percentage of ash of the coal, which may be entirely neglected in the calculation even if it should amount to, say, 20 per cent. Depending on the percentage of ash the weight of the combustion gases proper would change so that, at a per cent. of ash in the coal, instead of $1 + \epsilon \,.\, L_{th}$, it would be only $1 - a/100 + \epsilon \,.\, L_{th}$.

Influences Depending on the Operation of the Kiln.

Two further influences result from the operation of the kiln, viz., the combustion temperature and the daily capacity. From the remaining influences in this group, a normal coating on the lining of the kiln has been taken into consideration in preparing Diagram 4 on the shell losses on the rotary tube. The position of the flame and the presence of flue dust have been neglected, as well as the formation of rings. If one of these factors has a decisive influence on the heat consumption of the kiln, the case is one of abnormal operation which is not considered here.

MAXIMUM THEORETICAL COMBUSTION TEMPERATURE.—As in the case of the influence of water content, a greater range of changes will be examined on the influence of the maximum temperature and the daily capacity.

Without preheating, a theoretical temperature of 1,960 deg. C. can be obtained with an excess of air of 1·1 and a coal of 6,600 kcal. calorific value. Previously

a temperature of 2,200 deg. C. was fixed as a maximum limit; for each intermediate temperature there is obtained a new curve of flue-gas heat and from the intersection of the curve of heat required with the flue-gas heat line the corresponding temperature and the heat consumption. The values are:

Maximum temperature of flue gas (deg. C.)	1,960	2,000	2,040	2,080	2,120	2,160	2,200
Temperature of flue gas (deg. C.) ..	570	480	420	385	350	325	295
Heat required (kcal. per kg.) ..	2,260	1,960	1,730	1,660	1,550	1,470	1,395
Thermal efficiency (per cent.) ..	69·9	76·0	79·4	81·5	83·5	85·0	86·6

The figures of the heat required are shown in Fig. 10 over the maximum combustion temperatures. The factor for the influence of the maximum temperature is $-5{\cdot}9 + 6{\cdot}3$ for the kiln for which the calculation is made.

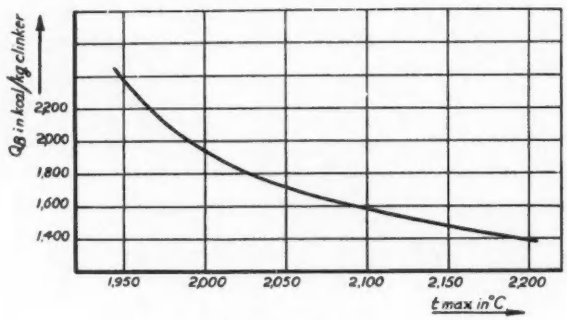

Fig. 10.

The increase of the temperature from 2,000 to 2,200 deg. C., which would result in a saving of heat of 28·7 per cent., is still possible if the losses on the cooler are kept low. The figure 1,395 kcal. per kg. would correspond to 21·2 per cent. of coal and 2·40 kg. flue gas per kg. clinker. Preheating of the air would have to be 85 kcal. per kg. flue gas, equivalent to 204 kcal. per kg. clinker. When the clinker contains 262 kcal. on entering the cooler there are still available 58 kcal. per kg. clinker for heat losses in the cooler and in the heat of the issuing clinker, which is easily obtainable with coolers arranged in prolongation of the kiln.

Here also it will be seen that the kiln in the example is relatively overloaded, so that its operating figures lie in the range of high factors. Without preheating and with higher figures of excess of air the capacity demanded is hardly obtainable. On the other hand, it would be of relatively less value to increase the temperature above 2,200 deg. C. The factor would then be only $\pm$ 2·40. The saving of heat, though still considerable, would be counterbalanced by difficulties in the construction of the kiln, which would be very costly.

OUTPUT.—It is recognised that the loading of the kiln has a special influence on the heat consumption, and the influence of the output per hour is also par-

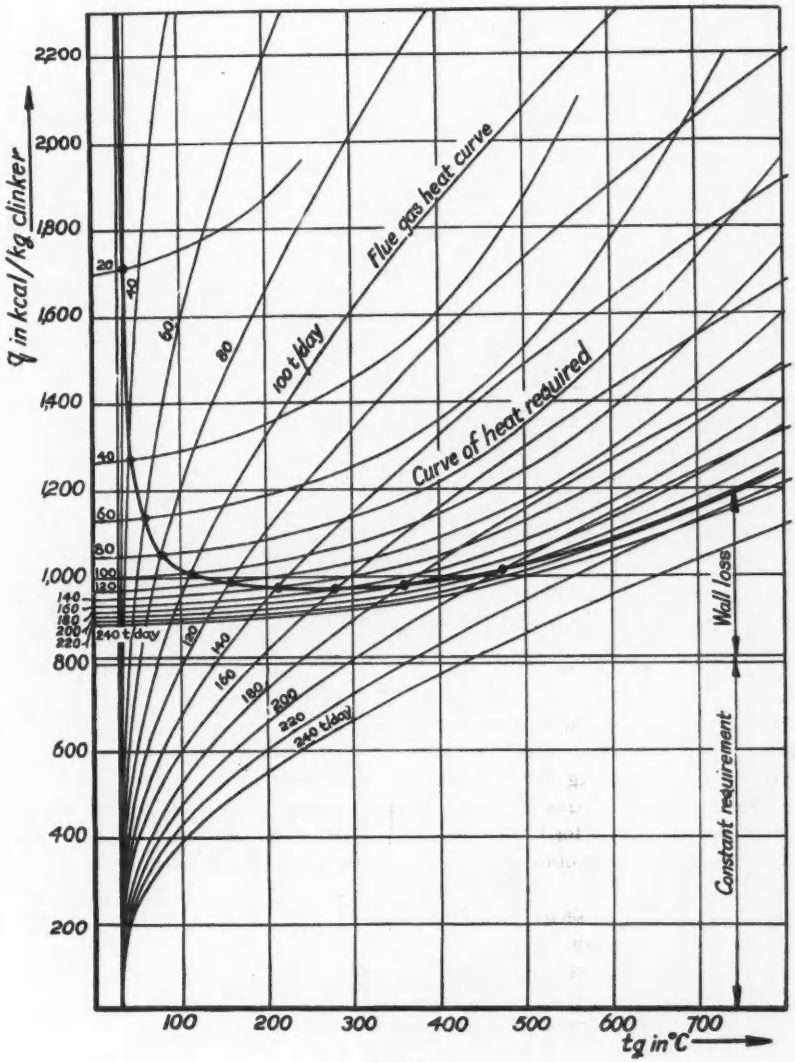
q in kcal/kg clinker
2200
2000
1800
1600
1400
1200
1,000
800
600
400
200
Flue gas heat curve
Curve of heat required
Wall loss
Constant requirement
100 t/day
240 t/day
100
200
300
400
500
600
700
tg in °C

Fig. 11.

ticularly interesting. Keeping the maximum temperature, used as basis, for all cases of loading, a calculation is obtained in which only the values for the shell loss per kg. of clinker and the ordinates of the curve of flue-gas heat have to be reduced in the ratio of the output per hour. Through the points of intersection of each two sets of curves, a line relating to the kiln under consideration may then be drawn, and its intersection with the curves of flue-gas heat enables the waste-gas heat temperatures to be found, and, by interpolation, also the intermediate values of the daily output.

For the example just dealt with, Fig. 13 and the following figures are obtained for a rotary kiln 3 m. by 60 m. at $t_{max} = 2{,}000$ deg. C. :

Output (tons per day)	40	80	120	160	200	210	215
Waste-gas temperature (deg. C.) ..	50	85	155	280	480	600	900
Heat consumption (kcal. per kg.) ..	1,600	1,400	1,450	1,595	1,960	2,300	3,510
Coal consumption (per cent.)	24·3	21·8	22·0	24·2	29·7	34·9	53·4
Thermal efficiency (per cent.) ..	97·5	95·8	92·4	86·0	76·0	70·0	55·0
Quality factor (per cent.)	99·5	98·7	97·9	95·0	90·0	84·4	67·2

These figures are plotted in Fig. 12. The curve of waste-heat temperatures shows that the values for the range of small outputs are only of theoretical interest. Only at a waste-gas temperature of about 75 deg. C. would the quantity of flue gas at full saturation be sufficient to carry off the steam from the raw material, so that 80 tons per day would therefore represent the lowest limit for the running of the kiln.

There is also a maximum limit because for more than 218 tons per day the curves of flue-gas heat and of heat requirement do not intersect, and the curves for the efficiencies reach zero for these outputs. The kiln is therefore at $t_{max} = 2{,}000$ deg. C. near this maximum limit of 200 tons output. If the ratio of the operating output to this maximum output is designated as loading of the kiln, the loading at 200 tons output is $200 \div 218 = 91{\cdot}6$ per cent. In spite of this high loading, which was already inferred from the size of the various factors, there is for the variation of the load a factor of only $\pm$ 1.55, from which it is concluded that a reduction of output is not the best means for reducing the heat consumption of the kiln. On the other hand, the curves for heat consumption and efficiency show that a further increase of output is hardly advisable, and that the daily output of 200 tons represents the practical limit for the kiln at 2,000 deg. C. maximum temperature. The curves for output below 160 tons are very flat, so that the range of 160 to 200 tons, i.e., a load of from 75 to 95 per cent., should be the most favourable for the kiln. Other examples with other maximum temperatures have shown that this measure of loading is the most favourable range for the standard output of the kiln.

Up to this limit the efficiencies remain high—the thermal efficiency lies between 75 and 86 per cent.—but below this limit they drop very rapidly. The compilation of Fig. 12 is therefore well adapted to the determination of the most favourable standard output of the kiln. It shows also that the kiln has an operating

point with minimum heat consumption which lies considerably below the normal operating point. Therefore the kiln will not be " too long " when there is a temporary reduction of output. With smaller units it may, however, happen that the kiln is operating close to the fuel minimum, and that an increase as well as a decrease of output causes an increase of fuel consumption.

Thermal efficiency and loading of the kiln are closely connected, so that the corresponding loading of the kiln may be estimated from the efficiency, and predicted for a possible increase of the output of the kiln.

In another example for a loading of the kiln from 65 to 90 per cent., the values for the thermal efficiency were between 75 and 88 per cent.

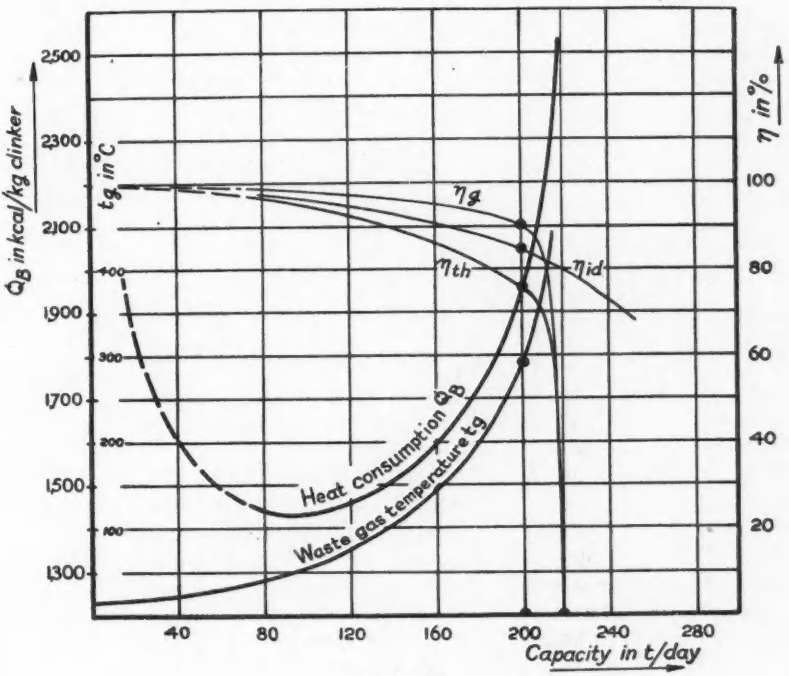

Fig. 12.

Structural Influences.

Of the influences attributable to changes in structural dimensions, a change of the internal surface of the kiln F_i must be particularly discussed. With a factor of $\pm 4{\cdot}1$ it is the next in importance after the maximum combustion temperature. This explains the great influence of interior fittings such as lifters and chains by which waste-gas temperatures have been successfully reduced. To a still greater extent the Lepol grate and the calcinator must therefore be

effective, as with these it is possible to increase the interior surface of the kiln by 30 to 40 per cent. instead of 10 to 12 per cent. maximum without at the same time seriously increasing the radiation loss.

Considering only the simple rotary kiln, an increase of the inner surface of the kiln is, except through interior fittings, possible only by an extension in a section of the length. The extension of the clinkering zone must, however, be avoided from the standpoint of the heat account. An extended clinkering zone permits an increase of the output and a reduction of the heat consumption, not because it improves the small kiln but because in practice a larger kiln is used. Because, however, the full capacity is not required the kiln is narrowed at the part where the inner surface of the kiln ought to be relatively the largest. The increase of the capacity of the small highly-loaded kiln made possible by the extension of the clinkering zone is at first sight attractive, but it is obtained by the unsuitable means of a reduction of the loading of the kiln and with its uneconomic use.

An extension of the kiln towards the feed end would have a better effect, because the increase of the outer surface would have practically no effect and could be neglected in the calculation; this, however, would not be permissible with an extended clinkering zone on account of the high temperatures in this part of the kiln.

There remains to be discussed only the thickness and the interior heat conductivity of the kiln lining, for which the factor ± 0.5 is obtained. Of the influences examined, this is the least important except one and if, in addition, we consider the great difficulties in the way of a decrease of the shell losses, then the benefit of this slight possibility of saving loses its last value.

To avoid misunderstanding, it may be mentioned that it is a question here only of the shell losses of the rotary tube proper, and not of the losses of the cooling drum too, whose alteration would influence the preheating of the combustion air and with it the maximum combustion temperature, and to which therefore, a higher factor is due. The influence of the maximum combustion temperature, as already determined, may be divided, and the influence of the excess-air factor and of the losses on the cooler may then be determined separately. There is then obtained the factors $+ 0.5$ and $- 0.8$ for the losses on the cooler, while the factor of excess air remains with ± 4.6, which is the largest of all the influences.

Order of Importance.

According to the size of the factor for the decrease of the heat consumption the importance of the various influences is in the following order: (1) Excess of air for combustion, (2) Internal surface of the kiln, (3) Clinkering temperature, (4) Daily output, (5) Shell losses of the cooler, (6) Water content of the raw material, (7) Shell losses of the rotary tube, (8) Calorific value of the coal.

The following factors have no influence: The ash content of the coal; Heat losses in the flue dust; Changes of normal operation (*a*) through caking and formation of rings, (*b*) through changes of the normal speed of rotation of the

kiln and cooler and of the normal relation between the contents and the output of the kiln, and (*c*) change of the position of the flame in the kiln.

If other kilns are calculated in this manner the same order of importance is obtained, except that the figures are generally smaller corresponding to the loading of the kiln. Higher loading of kilns will hardly be experienced, and for this reason higher factors for the influences will also be rare. Only the influence of the water content of the raw material, placed here in sixth place, can alter according to the normal water content, and for greater content of water and small output it may increase in importance to fourth place.

A slightly different order of importance is obtained if we investigate the question as to which particular influence may cause an increase of heat consumption. The clinkering temperature then takes first place, followed by excess of air, internal surface of the kiln, and daily output; in the fifth place is the water content, and lastly the shell losses of the cooler and of the rotary tube and the calorific value of the coal.

Final Observations on Fuel Consumption.

Examinations on the possibilities of a saving of fuel raise the point as to the limits of saving. The principal disadvantage of the older rotary kiln plants is the high heat losses in the cooler, from which follow uneconomic use of the heat of the clinker, low maximum temperatures, and therefore high heat losses of waste gas. If this disadvantage is removed and the maximum temperature near to the upper limit set by the kiln lining is attained, then a reduction of heat consumption by 20 to 25 per cent. can be secured. Beyond this, savings worth making are only possible if interior fittings or auxiliary apparatus are used, so that the temperature of the waste gas can be kept as low as the conveyance of the steam resulting from drying permits, and the heat consumption can be again heavily reduced.

Heat consumption figures of 700 to 1,000 kcal. for the dry process and 1,100 to 1,400 kcal. for the wet process can then be the rule, while for the rotary kiln without interior fittings or auxiliary apparatus hardly less than 1,000 and 1,400 kcal. respectively could be secured—and with a chemical efficiency of about 60 per cent. and a physical of about 80 per cent. quite important savings would be obtained.

Summary.

For the precalculation of the heat consumption of rotary kilns the old calculations lacked the possibility of calculating the waste-gas temperature and shell losses. With auxiliary figures which have been deduced from observations, a method of calculation has been worked out for rotary kilns for cement. From a comparison of different kilns several characteristic figures emerge from which information can be obtained on the most favourable normal capacity of a given rotary tube. In making the calculation the following particulars must be available: (1) Dimensions of the kiln and particulars of the interior fittings, chains, etc.; (2) daily output; (3) analysis of the raw mix; (4) water content of the raw material; and (5) calorific value of the coal.

Waste gas temperature and shell losses result from the co-ordinates of the point of intersection of curves of the heat required and of the flue gas heat, both of which are calculated for several waste-gas temperatures and plotted over these temperatures.

For the determination of the fuel consumption, with the help of the values found for waste-gas temperature and shell loss a formula is then set up compiling, without consideration of the processes in the kiln, the quantities of heat per kg. of clinker which leave and enter the rotary tube. For the determination of the heat consumption in figures the calculation can also be used to follow up the effect on the kiln of constructional and operating changes, changes in the raw material, and their effects on fuel consumption.

(*To be continued.*)

Estimation of Free Lime in Set Cement, Trass Cement, and Lime-Trass Mixtures. By V. RODT (*Zement*, No. 30, 1934).—The Lerch and Bogue process has been found suitable for determining the free lime in set cement and similar materials. The effect of the presence of water in the mixture due to the set binding material was investigated. It was found that up to one cc. water had no effect on the result. The quantities used were: cement 1 g., alcohol 30 cc., glycerine 6 cc., indicator 10 drops of 0.2 per cent. phenolphthalein; 1 cc. standard ammonium acetate = 0.0061 g. CaO. In practice the amount of water introduced with the material is 0.2 to 0.6 cc. When testing lime-trass mixtures 1 per cent. phenolphthalein must be used as indicator and the titration carried out after cooling to room temperature, otherwise low results are obtained due to absorption of the indicator by the trass. In general, calcium hydrate is set free during the hardening of cement and cement-trass mixtures. The amount of free lime is less at six months than at the commencement of hardening; this is probably due to carbonation. The amount of free calcium hydroxide in hardened specimens of blast-furnace cement is very small. The cement mixtures containing trass show considerable amounts of calcium hydrate not very different from the trass-free material. Large amounts of calcium hydrate go into combination in lime-trass mixtures. The combination is much more rapid at early ages (two weeks and one month) than later (six months). The amounts of lime taken up by the various trasses are not very different from one another and are not in accord with the strength figures. This leads to the conclusion that the combination of lime with trass is not the chief factor in hardening.

Research on Cement and Mortar.

THE following notes are from the annual report for the year 1933 of the Building Research Board of the Department of Scientific and Industrial Research (H.M. Stationery Office, price 2s. 6d.).

Effect of Carbon Dioxide on Strength of Mortars.

An investigation has been conducted into the effects of storing lime, lime-pozzolana, cement and cement-pozzolana mortars in an atmosphere of carbon dioxide. After preliminary curing in moist air, briquettes were stored in drums through which carbon dioxide or air free from carbon dioxide was passed. The humidity of the atmosphere was maintained at saturation, 80 per cent., and 50 per cent., in different series of tests. The briquettes were tested in tension, and their free lime and carbon dioxide contents were determined. For all types of mortar the rate of carbonation was slow in an atmosphere saturated with water vapour, but became more rapid at lower humidities. The effects of carbonation on strength vary somewhat in degree with the different types of mortars, but an increase of strength was found in most cases. Where carbonation was appreciable this increase of strength was very marked. With lime-pozzolana mortars containing a high proportion of pozzolana, extensive carbonation prevented to some extent the continued gain in strength over long periods which is observed in the absence of carbonation. Free lime is carbonated preferentially in all the materials studied, but the other hydrated calcium compounds (silicates and aluminates) are also readily carbonated.

These results indicate that considerable care must be taken to exclude atmospheric carbon dioxide in the air storage of small specimens for long period strength tests.

Chemical Resistance of Mortars and Concretes.

An investigation has been made of the mechanism of the action of sulphate solutions on set Portland cement. Tests of the expansion of mortar rods in solutions of sodium and magnesium sulphates have yielded some interesting results. It is known that the resistance of set cement products to sulphate attack can be increased by autoclaving under steam pressure in suitable conditions to such an extent that they become almost immune. But as this treatment is believed to alter the form of the hydrated calcium silicate and aluminate compounds present, and to cause the free calcium hydroxide to react with a siliceous aggregate, it is difficult to estimate from this result alone the relative importance of these changes. Tests have indicated that neither removal of the free calcium hydroxide nor the change of the hydrated silicates and aluminates by autoclaving is alone sufficient to do more than partially increase resistance to sulphate action. When both occur together the improvement is great.

Pozzolanas.

The substitution of pozzolana for cement reduces the strength at early ages, but this loss is steadily recovered with increasing age and the ultimate strength

is increased when the proportion of pozzolana is not too high. Data are at present available up to one year, and show that the strength at this age is increased by the substitution of 20 per cent. of pozzolana for cement and slightly reduced by the substitution of 40 per cent. From the form of the strength-age curves it seems probable, however, that the strength of the mix containing 40 per cent. of pozzolana will also ultimately exceed that of the mix containing cement alone. It may be noted that the strengths given by pozzolana-cement mixtures when tested in 1 : 3 standard sand mortars of dry consistence furnish even less indication of the strength of concrete than do similar tests on normal cement mixes.

The strength developed in pozzolana concretes, when expressed as a percentage of the strength of the plain cement mixes, varies somewhat with different Portland cements and the same pozzolana. No relation has yet been traced between this variation and the composition of the cement.

The permeability of pozzolana concretes at ages of two months and one year has been found to be the same as, or slightly less than, that of the corresponding concrete made from the plain cement. This has been found to hold for pozzolana contents up to 40 per cent.

Tests carried out on pozzolana cement concretes by the adiabatic calorimetric method show that the substitution of artificial pozzolanas for cement reduces the heat evolution during setting and hardening, but that the reduction is less than that calculated from the decrease in the Portland cement content of the mix. This is attributed to the evolution of some heat during the reaction of the pozzolana with the free calcium hydroxide present in the set cement.

Work has been continued on the resistance of mortars and concretes containing artificial pozzolanas to sea-water and sulphate solutions. The results confirm the previous conclusion that an increased resistance to sulphate action is obtained by the use of these pozzolanas. A further series of tests has been commenced on pozzolana mortars and concretes immersed in solutions of various salts and weak acids encountered in industrial processes.

Manufacture of Cement on a Forced-Draught Grate. By E. SCHIRM (*Zement*, No. 23, 1934).—A mixture of slurry and fuel is fed on to a grate to the underside of which suction is applied. The fuel is ignited and the raw material clinkered as it passes slowly with the moving grate. The surface of the grate is protected by a thin layer of clinker which is fed on to it at the same time as the raw material.

Another method is described in which the raw material is burnt in two stages. Three layers are fed on to the grate, (1) a thin layer of protective clinker, (2) a layer of raw material and fuel, and (3) a layer of decarbonated raw material and fuel. The amount of fuel in the second layer is just sufficient to decarbonate the slurry and that in the third layer to clinker the already decarbonated material. The products are discharged on to a sieve, and the second layer is fed back again to form the third layer which is then clinkered.

Abstracts from the Foreign Press.

Action of Water on Portland Cement. By L. CHASSEVENT (*Zement*, No. 17, 1934.)—The formation of calcium hydrosilicate has been studied by solutions of mixtures of calcium hydroxide and silicate acid. Silicic acid coagulates immediately in strong calcium hydroxide solutions, hence in mixtures of this type no silicic acid appears in the filtrate. Calcium hydroxide and silicic acid combine to form $CaO.SiO_2.aq$. The hydrolysis of monocalcium hydrosilicate produces a lime solution which can coagulate further silicic acid according to the amount of lime it contains. This explains the hardening of substances which contain a large amount of soluble silica, such as pozzolana and granulated slag which are mixed with small amounts of lime or Portland cement.

Heat Loss from Rotary Kiln Shells. By Mr. TOYOFUJIMARU (*Zement*, No. 24, 1934).—It is stated that the best method of reducing heat loss from a kiln is to use thick firebrick to obtain better insulation. Reduction of the radiation coefficient by using a polished casing for the kiln results in too high a temperature of the kiln shell. A further saving is obtained by raising the temperature of the air surrounding the shell by enclosing a portion on the kiln in a protective envelope.

Estimation of Alkalis in Cement. By W. MARSCHNER (*Zement*, No. 24, 1934).—SiO_2 is separated after one evaporation with HCl. R_2O_3 and CaO are removed from the filtrate by ammonia and ammonium oxalate. The filtrate is evaporated to 50 cc., small amounts of ammonia and ammonium oxalate are added, and the precipitate filtered off. This process must be carried out twice on each gram of cement. The filtrates are combined, evaporated, and the ammonium salts driven off. The residue is taken up with the least amount of water and magnesia precipitated in the cold with $Ba(OH)_2$ solution (0.2 g. $Ba(OH)_2$ in 5 cc. water for each gram of cement). After standing for half an hour the solution is filtered and the precipitate washed with 5 per cent. $Ba(OH)_2$ solution. Excess barium is removed with ammonium carbonate, the precipitate being washed by decantation and then on the filter with distilled water. The filtrate is evaporated on the water bath and heated to 130 deg. C. The residue is moistened with HCl and the alkalis (NaCl and KCl) weighed after driving off the excess HCl. For obtaining the amount of potassium the usual perchlorate method is used. This process is claimed to save time and to give a more accurate result than the usual method which tends to give too high a value due to contamination with sulphate.

Heat Insulation of Rotary Kilns. By P. P. Collada (*Tonindustrie Zeitung*, No. 44, 1934).—Difficulty experienced with insulating layers between the firebrick lining and the shell of rotary kilns has led to the abandonment of this type of insulation. The insulating layer either gets loosened and/or reduced to powder. In one case where kieselguhr was used for the insulating layer there was corrosion of the kiln shell. This was traced to the catalytic action of kieselguhr and the initial iron oxide of the shell on the sulphur dioxide in the flue gas. The product was sulphuric anhydride, which attacked the shell. Iron sulphate was found in the products of corrosion, together with iron oxide formed by its decomposition by heat from the kiln.

The Choice of Rotary Kiln Linings. By P. Budnikoff and S. A. Schicharewitsch (*Tonindustrie-Zeitung*, No. 7, 1934).—Special care must be exercised in the choice of linings for kilns making Portland cement from gypsum and clay with the simultaneous production of sulphuric acid. Tests were carried out on various refractories to ascertain their suitability in practice. Cubes of 70 mm. side were cut out of the lining blocks and a cylindrical hole 35 mm. in diameter and 30 mm. deep was bored out of each cube. The raw mix consisting of gypsum, clay, and coke was rammed into this cavity, the specimen raised slowly to 1,450 deg. C. in twenty-two hours and kept at this temperature for two hours. After the test the block was broken in half and examined. Bricks of Latino clay, Tschassov-Jar and Latino clay, Dinas clay (specific gravity 2·38, 2·42, and 2·49), and quartz were attacked by the mixture. Those of kaolin-fireclay, magnesite, black Dinas, and chromite-magnesite stood up well to the test. The best brick appears to be one in which the Al_2O_3 content is at least 42 per cent., the shrinkage after two hours heating at 1,450 deg. C. not greater than 0·5 per cent., and the porosity not greater than 8 per cent.

Loss of Heat in Flue Gas from Shaft Kilns. By F. ERDMANN (*Zement*, No. 21, 1934).—A method is described by which excess air can be calculated from the Orsat analysis without reference to the amount of coke used. From the Orsat analysis and excess air the efficiency of burning can be calculated. Tables are given for obtaining the amount of flue gas ex-water and the loss of heat due to flue gas, CO_2, and water vapour.

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